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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A61L 9/01		A2	(11) International Publication Number: WO 98/26808 (43) International Publication Date: 25 June 1998 (25.06.98)
(21) International Application Number: PCT/US97/22576 (22) International Filing Date: 9 December 1997 (09.12.97) (30) Priority Data: 60/033,649 17 December 1996 (17.12.96) US		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
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(54) Title: ABSORBENT ARTICLES WITH ODOR CONTROL SYSTEM			
(57) Abstract			
<p>The present invention comprises compositions and articles such as catamenials, diapers, pantiliners, adult incontinence garments, and underarm shields which minimize odor caused by body fluids and which optionally provide a pleasant scent signal to indicate that the odor is being removed. The odor control is provided by a combination of (1) material that inhibits the formation of odor that has at least one attribute selected from the group consisting of antimicrobial activity, urease inhibition activity, pH adjustment activity, and mixtures thereof; and (2) odor-absorbing material for objectionable odor molecules selected from the group consisting of: cyclodextrin; zeolite; activated carbon; kieselguhr; acid salt forming materials; and mixtures thereof. The scent signal is provided by cyclodextrin/perfume inclusion complexes and/or matrix perfume microcapsules to assure the wearer that the product is working.</p>			

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ABSORBENT ARTICLES WITH ODOR CONTROL SYSTEM

TECHNICAL FIELD

The present invention relates to an improvement in absorbent articles such as catamenials, diapers, and adult incontinence garments, with a system for malodor control and, optionally, a means to provide a "scent signal" in the form of a pleasant odor which signals the removal of odor during use of the product. The odor-absorbing system herein is designed to combat a broad spectrum of odoriferous materials, including sour "ammonia-type" odors.

BACKGROUND OF THE INVENTION

A wide variety of fluid absorbent structures known in the art absorb body fluids such as blood, urine, menses, and the like, and are sanitary and comfortable in use. Disposable products of this type generally comprise fluid-permeable topsheet material, fluid absorbent core, and fluid-impermeable backsheet material. Various shapes, sizes and thicknesses of such articles have been explored in an attempt to make their use more comfortable and convenient.

Odor control in sanitary products has been under investigation for many years. Many body fluids have an unpleasant odor, or develop such odors when in contact with air and/or bacteria for prolonged periods.

Various odor-controlling materials have been disclosed in the literature. For example, U.S. Pat. No. 4,525,410, Hagiwara et al., issued June 25, 1985, teaches zeolite particles (doped with bactericidal cations) assertedly stably held in a fibrous web by incorporating some portion of meltblown fibers in the web, and applying heat. These compositions can be used as the "outside cover layer" in, e.g., "general sanitary goods."

U.S. Pat. No. 2,690,415, F. A. Shuler, issued Sept. 28, 1954, teaches particles of odor-absorbing materials uniformly affixed at the interstices of a permeable web by adhesive to provide an odor absorbent medium for, e.g., catamenials. Particulate carbon, silica gel and activated alumina are noted. Shifting/displacement of the particulates is assertedly avoided and the sheet is flexible.

ABSCENTS (odor-control molecular sieve from Union Carbide) for use in diapers and catamenials are specifically noted in Union Carbide brochure (A. J. Gioffre 1988). The brochure indicates that UC's market research shows potential benefits in such products. U.S. Pat. Nos. 4,795,482 and 4,826,497, relate to ABSCENTS used as an odor-controlling material, generally, and in sanitary products, in particular.

Zeolitic materials are generally quite safe, and while they do effectively control many odors associated with body fluids, unfortunately, they do not provide optimal control for ammonia odor and similar odors, presumably associated with short-chain amines and/or urea. This is particularly true of the so-called "high ratio" ($\text{SiO}_2:\text{AlO}_2$) odor-controlling zeolites. Certain "intermediate ratio" ($\text{SiO}_2:\text{AlO}_2$) zeolites are more effective for adsorbing amine-type odors.

Also, some consumers prefer catamenial and diaper products, etc., that have a "scent signal" in addition to odor control. A "scent signal" is a positive perfume odor which signals the removal of odor during use of the product. This scent signal is normally difficult to provide because odor absorbents can react with and/or deplete the perfume in the article prior to use, and the absorbents themselves can become inactive.

SUMMARY OF THE INVENTION

The present invention provides an improvement to the art by incorporating odor-absorbing materials for malodor control and materials that are antibacterials and/or urease inhibitors to minimize the formation of such odors. The combination of these two approaches in an odor control system has been found to be the most effective way to combat odor. In addition, the compositions and articles herein can also contain moisture-activated encapsulated perfumes for an in-use "burst of fragrance" or "scent signal," into absorbent compositions and articles of manufacture.

Therefore, the present invention relates to absorbent compositions which minimize the odor that can be caused by bodily fluids and which optionally, but preferably, provide a scent signal indicating that the odor is being removed, comprising:

- I. an effective amount of material that inhibits the formation of odor that has at least one attribute selected from the group consisting of antimicrobial activity, urease inhibition activity, pH adjustment activity, and mixtures thereof;
- II. an effective amount of odor-absorbing material for objectionable odor molecules, said odor absorbing material preferably being selected from the group consisting of:
 - A. cyclodextrin;
 - B. zeolite;
 - C. activated carbon;
 - D. kieselguhr;
 - E. acid salt forming materials; and
 - F. mixtures thereof;

- III. optionally, an effective amount of moisture-activated encapsulated perfume; and
- IV. an effective amount of fluid absorbing material.

The present invention also relates to consumer articles of manufacture containing the above compositions, such as diapers, catamenials, pantiliners, adult incontinence garments, and underarm shields, which decrease odors associated with bodily fluids such as blood, urine, and the like, and which provide a pleasant scent signal.

DETAILED DESCRIPTION OF THE INVENTION

The compositions and methods for odor control involve the use of odor-controlling and odor-absorbing material, as described more fully hereinafter.

The articles which employ said compositions of odor-controlling and odor-absorbent materials and moisture-activated encapsulated perfumes can be prepared using constituents that are well-known in current commercial practice. For the types of articles, reference is made to the general sanitary products patent literature and trade catalogues for such items. Such items typically comprise a moisture absorbent "core" (e.g., pad) interposed between a "topsheet" and a "backsheet." Likewise, methods and apparatus for assembling disposable diapers, catamenials, and the like are known in the art.

The various individual constituents used in the assembly of catamenials, disposable diapers, and the like, are well-known. The present invention relates to the novel combination of odor-controlling materials and odor-absorbent materials as constituents of such articles.

(I) ANTIMICROBIALS AND/OR UREASE INHIBITORS

The absorbent compositions contains an effective amount of urease inhibitor and/or antimicrobials.

Metallic Salts

The absorbent compositions products of the present invention are prepared by contacting the solid absorbent compositions material with, preferably, an aqueous solution of the antimicrobial and/or urease inhibitor, preferably transition metal ion. Suitable sources of the transition metal ions are their soluble salts. The preferred salts are silver, copper, zinc, ferric, and aluminum salts, more preferably zinc. It is also desirable that the anion provide some benefit. E.g., the anion can have the ability to provide urease inhibition, such as borate, phytate, etc. Suitable examples are silver chloride, silver nitrate, mercury acetate, mercury chloride, mercury nitrate, copper metaborate, copper bromate, copper bromide, copper chloride, copper dichromate, copper nitrate, copper salicylate, copper sulfate, zinc acetate, zinc borate, zinc phytate,

zinc bromate, zinc bromide, zinc chlorate, zinc chloride, zinc sulfate, cadmium acetate, cadmium borate, cadmium bromide, cadmium chlorate, cadmium chloride, cadmium formate, cadmium iodate, cadmium iodide, cadmium permanganate, cadmium nitrate, cadmium sulfate, and gold chloride. Other salts that have been disclosed as having urease inhibition properties include ferric and aluminum salts, especially the nitrates, and bismuth salts. Zinc salts are preferred.

The preferred, metallic salt, preferably water-soluble zinc salts, can be added to the solution used to prepare the absorbent compositions of the present invention. A water-soluble metallic salt can be used as an odor control material. A water-soluble metallic salt can be present in the freshening composition of the present invention to absorb amine and sulfur-containing compounds. Furthermore, they usually do not contribute an odor of their own. Preferably the water-soluble metallic salts are selected from the group consisting of copper salts, zinc salts, and mixtures thereof.

The preferred zinc salts have been used most often for their ability to ameliorate malodor, e.g., in mouth wash products, as disclosed in U.S. Pat. Nos. 4,325,939, issued Apr. 20, 1982 and 4,469,674, issued Sept. 4, 1983, to N. B. Shah, et al., incorporated herein by reference. U.S. Pat. No. 3,172,817, issued to Leupold, et al., discloses deodorizing compositions containing slightly water-soluble salts of an acyl-acetone with a polyvalent metal, including copper and zinc salts. Said patents are incorporated herein by reference.

Examples of preferred water-soluble zinc salts are zinc chloride, zinc gluconate, zinc lactate, zinc maleate, zinc salicylate, zinc sulfate, etc. Highly-ionized and soluble zinc salts such as zinc chloride, provide the best source of zinc ions. Examples of preferred copper salts are copper chloride and copper gluconate. Preferred metallic salts are zinc chloride and copper chloride.

Metallic salts are added to the absorbent composition of the present invention typically at a level of from about 0.001% to about 1%, preferably from about 0.002% to about 0.7%, more preferably from about 0.03% to about 0.5%, by weight of the absorbent compositions.

Urease Inhibitors

There are many materials that exhibit urease inhibition and/or suppression. A partial list of materials that have been disclosed as inhibitors includes the metallic salts listed above; hydroxamic acid, modified hydroxamic and/or dihydroxamic acids, e.g., substituted with various hydrocarbon groups such as acyl, e.g., aceto-, chloronitrobenzamidoaceto-, and nitrobenzamidoaceto- (e.g., 2-para), C₁-21 alkyl, aryl, and/or alkaryl groups, cycloalkyl (e.g., cyclohexyl), peptidyl, naphthoxy-alkane, and

their salts; thiourea; hydroxylamine; salts of phytic acid, especially sodium, potassium, calcium, and magnesium; extracts of plants of various species, including various tannins, e.g. carob tannin, and their derivatives such as chlorogenic acid derivatives; naturally occurring acids such as ascorbic acid, citric acid, and their salts; phenyl phosphoro diamide/diamino phosphoric acid phenyl ester; metal aryl phosphoramidate complexes, including substituted phosphorodiamide compounds; phosphoramidates without substitution on the nitrogen; boric acid and/or its salts, including especially, borax, and/or organic boron acid compounds; the compounds disclosed in European Patent Application 408,199, incorporated by reference; sodium, copper, manganese, and/or zinc dithiocarbamate; quinones; phenols; thiurams; substituted rhodanine acetic acids; alkylated benzoquinones; formamidine disulphide; 1:3-diketones maleic anhydride; succinamide; phthalic anhydride; pheinic acid; N,N-dihalo-2-imidazolidinones; N-halo-2-oxazolidinones; thio- and/or acyl- phosphoryltriamide and/or substituted derivatives thereof; thiopyridine-N-oxides, thiopyridines, and thiopyrimidines; oxidized sulfur derivatives of diaminophosphinyl compounds; cyclotriphosphazatriene derivatives; ortho-diaminophosphinyl derivatives of oximes; bromo-nitro compounds; S-aryl and/or alkyl diaminophosphorothiolates; diaminophosphinyl derivatives; mono- and/or poly-phosphorodiamide; 5-substituted-benzoxathiol-2-ones; N-(diaminophosphinyl)arylcarboxamides; alkoxy-1,2-benzothiazin compounds; etc.

As stated above, a large number of urease inhibitors are known, some having been purposefully synthesized by the pharmaceutical industry, and others whose original use was for purposes outside the realm of urease inhibition, but which can also be suitably employed to act as structural mimics of urea. These latter compounds include low molecular weight, water soluble materials which act as an irreversible substrate or modifier of the active site of the urease enzyme.

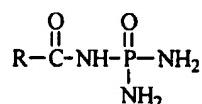
Among the low molecular weight urease inhibitors that are thought to serve as substrate mimics are hydroxamic acid and the substituted hydroxamic acids mentioned above. Acetohydroxamic and propionhydroxamic acid are the most common of the acyl substituted hydroxamic acids. These two compounds, as well as the parent hydroxamic acid and the alkali or alkaline earth salts of said acids, are particularly efficacious in inhibiting urease enzyme activity *in vitro*.

A variety of phosphorus compounds, including those disclosed hereinbefore, have been prepared for *in vivo* reduction in urease activity. Many of the pharmaceutical industry generated products are compatible with the environment due to their biodegradability and the structure and oxidation state of the phosphorus containing moiety.

In particular, phosphorus triamides of the general formula:

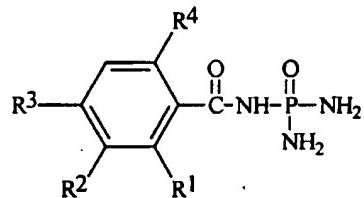


wherein R is hydrogen, phenyl, substituted phenyl, alkyl, alkenyl, and other suitable moieties or preferably N-(diaminophosphinyl)arylcarboxamides of the formula:

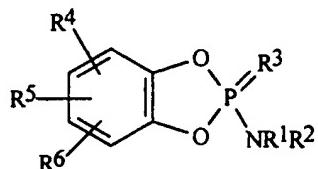


wherein R is 3-pyridyl, 2-furanyl, 2-naphthyl, cinnamyl, benzyl, phenyl, and substituted phenyl are efficacious as urease inhibitors when added in a sufficient amount to inhibit the enzyme urease.

Other preferred urease inhibitors have the general formula:



where R¹, R², R³, and R⁴ is more preferably hydrogen, nitro, halogen, amino, C₁₋₄ alkyl, C₁₋₄ alkoxy, trifluormethyl, cyano, phenoxy, phenyl, and mixtures thereof. A further embodiment of the present invention includes urease inhibitors of the general formula:



wherein;

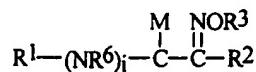
R¹ and R² are the same or different and are hydrogen or alkyl having from 1 to about 4 carbon atoms;

R³ is oxygen or sulfur; and

R⁴, R⁵ and R⁶ are the same or different and are hydrogen, alkyl, arylamino, diarylamino, halogen, hydroxy, mercapto, alkylmercapto, alkyl mercapto, O-diaminophosphinyl, S-diaminophosphinyl, N-diaminophosphinyl, diaminophosphonyl, amino, cyano, nitro, alkylamino, dialkylamino, arylmercapto, isocyano, isocyanato, trihalomethyl, alkoxy, thiocyano, alkanoyl, or any two R⁴, R⁵ and R⁶ group taken together may form an alkylene or alkenylene chain which may optionally include one or more divalent oxygen, nitrogen, or sulfur moieties forming a 3,4,5 or 6 membered fused ring structure.

A variety of nitrogen containing compounds have been prepared for *in vivo* use against urease activity. These materials are effective urease inhibitors when used *in vivo* in the present invention.

The present invention also relates to a composition and method of inhibiting urease activity comprising an effective amount of one or more oxime compounds having the formula



wherein R¹ and R² are independently selected from the group consisting of alkyl, aryl, and heteroaryl, or R¹ and R² may be covalently bonded together to form a cyclic alkyl; M is selected from the group consisting of =O, =S, -SR⁴ and -OR⁴ (when M is -OR⁴ or -SR⁴, there is a hydrogen bonded to the carbon to which M is bonded and R⁴ is selected from the group consisting of hydrogen, alkyl, aryl and heteroaryl); R³ is selected from the group consisting of hydrogen, alkyl, aryl and heteroaryl; R⁶ is selected from the group consisting of hydrogen, alkyl, aryl and heteroaryl; and i is selected from the group consisting of 1 and 0.

When R¹ is aryl, it is preferably selected from substituted and unsubstituted, preferably 2-furanyl, 3-furanyl, 2-thienyl, 3-thienyl, 2-pyrrolyl, 3-pyrrolyl and phenyl. Also preferred are these aryl substituted with C₁-C₆ alkyl, C₁-C₆ alkoxy, amino, halogen, hydroxy, mercapto, alkyl mercapto, O-diamino-phosphinyl, S-diamino-phosphinyl, diaminophosphinyl, diaminophosphonyl, cyano, nitro, alkylamino, di-alkylamino, aryl mercapto, isocyanato, trihalomethyl, alkoxy, thiocyanato, and alkanoyl. When R¹ is alkyl, it is preferably selected from substituted and unsubstituted, preferably unsubstituted C₁-C₁₈ alkyl, more preferably C₁-C₁₂ straight chain.

When R² is aryl, it is preferably selected from substituted and unsubstituted, preferably 2-furanyl, 3-furanyl, 2-thienyl, 3-thienyl, 2-pyrrolyl, 3-pyrrolyl and phenyl. Also preferred are these aryl substituted with C₁-C₆ alkyl, C₁-C₆ alkoxy, amino, halogen, hydroxy, mercapto, alkyl mercapto, O-diamino-phosphinyl, S-diamino-phosphinyl, diaminophosphinyl, diaminophosphonyl, cyano, nitro, alkylamino, di-alkylamino, aryl mercapto, isocyanato, trihalomethyl, alkoxy, thiocyanato, and alkanoyl. When R² is alkyl, it is preferably selected from substituted and unsubstituted, preferably unsubstituted C₁-C₁₈ alkyl, more preferably C₁-C₁₂ straight chain.

When R³ is aryl, it is preferably substituted or unsubstituted phenyl. When R³ is alkyl, it is preferably selected from substituted and unsubstituted, preferably unsubstituted C₁-C₁₈ alkyl, more preferably C₁-C₁₂ straight chain. R³ is most preferably hydrogen.

When R⁴ is aryl, it is preferably substituted or unsubstituted phenyl. When R⁴ is alkyl, it is preferably selected from substituted and unsubstituted, preferably unsubstituted C₁-C₁₈ alkyl, more preferably C₁-C₁₂ straight chain. R⁴ is most preferably hydrogen.

When R⁶ is aryl, it is preferably substituted or unsubstituted phenyl. When R⁶ is alkyl, it is preferably selected from substituted and unsubstituted, preferably unsubstituted C₁-C₁₈ alkyl, more preferably C₁-C₁₂ straight chain. R⁶ is most preferably hydrogen.

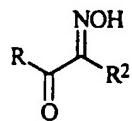
Suitable compounds for use in the present invention include syn- and anti-forms or mixtures thereof.

In particular, oximes of the general formula:



wherein R is hydrogen; or R and R² are the same or different C₁-C₂₂ alkyl and branched alkyl, C₁-C₂₂ alkenyl or branched alkenyl; an aryl group substituted with one or more amino; heterocyclic rings, preferably 2-furanyl, substituted 2-furanyl, 3-furanyl, and substituted 3-furanyl wherein the furanyl substituents are one or more alkyl, amino, cyano, nitro, alkylamino, dialkylamino, aryl mercapto, isocyanato, trihalomethyl, alkoxy, thiocyano, alkanoyl and halogen moieties; in the case where two aryl or two heterocyclic rings or one of each are present that contain more than one substituent, for example, when R or R² each comprise an aryl or heterocyclic ring such as a 2,4-dichlorofuranyl, 2-chloro-4-methylfuranyl, or a tri-substituted heterocyclic moiety such as 3,4,5-trichlorofuranyl; or R and R² taken together may form an alkylene or alkenylene chain which may optionally include one or more divalent oxygen, nitrogen, or sulfur moieties forming a 3, 4, 5 or six membered fused ring structure; are efficacious as urease inhibitors in a toilet bowl cleaner and flush tank additive when added in an amount sufficient to inhibit the enzyme urease.

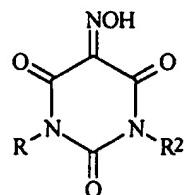
In particular, keto oximes of the general formula:



wherein R is hydrogen; or R and R² are the same or different C₁-C₂₂ alkyl and branched alkyl, C₁-C₂₂ alkenyl or branched alkenyl; aryl groups substituted by one or more halogen, hydroxy, mercapto, alkyl mercapto, O-diaminophosphinyl, S-

diaminophosphinyl, diaminophosphinyl, diaminophosphonyl, amino, cyano, nitro, alkylamino, dialkylamino, aryl mercapto, isocyanato, trihalomethyl, alkoxy, thiocyano, alkanoyl; or R and R² taken together may form an alkylene or alkenylene chain which may optionally include one or more divalent oxygen, nitrogen, or sulfur moieties forming a 3, 4, 5 or six membered fused ring structure; R and R² each comprise a heterocyclic ring, preferably 2-furanyl, substituted 2-furanyl, 3-furanyl, and substituted 3-furanyl; are efficacious as urease inhibitors when added in an amount sufficient to inhibit the enzyme urease. The furanyl substituents can be substituted by one or more alkyl, amino, cyano, nitro, alkylamino, dialkylamino, aryl mercapto, isocyanato, trihalomethyl, alkoxy, thiocyano, alkanoyl and halogen moieties and mixtures thereof. For example, R or R² may each comprise the same or different di-substituted aryl or heterocyclic moiety such as 2,4-dichlorofuranyl, 2-chloro-4-methylfuranyl, or a tri-substituted moiety such as 2,4,6-trichlorophenyl, or 3,4,5-trichlorofuranyl.

Also surprisingly efficacious as a urease inhibitor when added in an amount sufficient to inhibit the enzyme urease is violuric acid and derivatives of violuric acid having the general formula:



wherein R and R² can be the same or different and are hydrogen, C₁-C₂₂ alkyl and branched alkyl, C₁-C₂₂ alkenyl or branched alkenyl; an aryl or heterocyclic ring substituted by one or more amino, halogen, hydroxy, mercapto, alkyl mercapto, O-diaminophosphinyl, S-diaminophosphinyl, diaminophosphinyl, diaminophosphonyl, cyano, nitro, alkylamino, dialkylamino, aryl mercapto, isocyanato, trihalomethyl, alkoxy, thiocyano, alkanoyl or mixtures thereof.

The urease inhibitor is included in the absorbent composition of the present invention in an effective amount to provide an odor improvement. The term "effective amount" as used herein, means a level sufficient to inhibit, or significantly reduce the hydrolysis of urea for a specific amount of time that is related to the expected time that the article will exist with urea present. Such a time is at least about 2 hours, and preferably the effect should be noticeable at longer times, e.g., overnight, or even several days, if the article is stored until final disposal can take place. Preferred levels of urease inhibitor are from about 0.0002% to about 2%, preferably from about 0.002% to about

0.5%, and most preferably from about 0.01% to about 0.3%, by weight of the composition.

Antimicrobials

Organic antimicrobials can also be used in the present invention. It is preferable to use a broad spectrum antimicrobial, e.g., one that is effective on both bacteria (both gram positive and gram negative) and fungi. A limited spectrum antimicrobial, e.g., one that is only effective on a single group of microorganisms, e.g., fungi, can be used in combination with a broad spectrum antimicrobial or other limited spectrum antimicrobials with complimentary and/or supplementary activity. A mixture of broad spectrum antimicrobials can also be used.

Antimicrobial antimicrobials useful in the present invention can be biocidal compounds, i.e., substances that kill microorganisms, or biostatic compounds, i.e., substances that inhibit and/or regulate the growth of microorganisms.

Preferred antimicrobial antimicrobials are those that are water-soluble and are effective at low levels because the organic antimicrobials can form inclusion complexes with the preferred cyclodextrin molecules in the treatment solution used to form the animal litter, thus rendering the complexed antimicrobials much less effective. Water-soluble antimicrobials useful in the present invention are those that have a solubility in water of at least about 0.3 g per 100 ml of water, i.e., about 0.3% at room temperature, preferably greater than about 0.5% at room temperature. These types of antimicrobials have a lower affinity to the cyclodextrin cavity, at least in the aqueous phase, and are therefore more available to provide antimicrobial activity. Antimicrobials with a water-solubility of less than about 0.3% and a molecular structure that readily fits into the cyclodextrin cavity, have a greater tendency to form inclusion complexes with the cyclodextrin molecules, thus rendering the antimicrobial less effective to control microbes in the cyclodextrin solution. Therefore, many well known antimicrobials such as short chain alkyl esters of p-hydroxybenzoic acid, commonly known as parabens; N-(4-chlorophenyl)-N'-(3,4-dichlorophenyl) urea, also known as 3,4,4'-trichlorocarbanilide or triclocarban; 2,4,4'-trichloro-2'-hydroxy diphenyl ether, commonly known as triclosan are not preferred in the present invention since they are relatively ineffective when used in conjunction with cyclodextrin.

The water-soluble antimicrobial is included in the absorbent composition of the present invention in an effective amount. The term "effective amount" as herein defined means a level sufficient to significantly inhibit, or prevent growth of microorganisms for a specific period of time, as discussed above. Preferred levels of antimicrobial are from

about 0.0005% to about 0.5%, more preferably from about 0.001% to about 0.3%, most preferably from about 0.003% to about 0.1%, by weight of the composition.

The antimicrobial can be any organic antimicrobial material. Alkyl monocarboxylic acids having from about 3 to about 9 carbon atoms and halogenated aromatic hydrocarbons, e.g., halogenated phenols, halogenated diphenyls and halogenated bis-phenols such as para-chloro-meta-cresol, hexachlrophene, 2,4,4'-trichloro-2'-hydroxydiphenyl ether, trichlorocarbanalide, 2,4-dichloro-meta-xylenol, 3,4,5-tribromosalicylanalide, 3,5,3',4'-tetrachlorosalicylanalide, and mixtures thereof, can be used. Preferred water-soluble antimicrobials include organic sulfur compounds, halogenated compounds, cyclic organic nitrogen compounds, low molecular weight aldehydes, quaternary compounds, dehydroacetic acid, phenyl and phenoxy compounds, and mixtures thereof.

Non-limiting examples of the preferred water-soluble antimicrobials for use in the present invention include a mixture of about 77% 5-chloro-2-methyl-4-isothiazolin-3-one and about 23% 2-methyl-4-isothiazolin-3-one, a broad spectrum antimicrobial available as a 1.5% aqueous solution under the trade name Kathon® CG by Rohm and Haas Co.; 5-bromo-5-nitro-1,3-dioxane, available under the trade name Bronidox L® from Henkel; 2-bromo-2-nitropropane-1,3-diol, available under the trade name Bronopol ® from Inolex; 1,1'-hexamethylene bis(5-(p-chlorophenyl)biguanide), commonly known as chlorhexidine, and its salts, e.g., with acetic and digluconic acids; a 95:5 mixture of 1,3-bis(hydroxymethyl)-5,5-dimethyl-2,4-imidazolidinedione and 3-butyl-2-iodopropynyl carbamate, available under the trade name Glydant Plus® from Lonza; N-[1,3-bis(hydroxymethyl)2,5-dioxo-4-imidazolidinyl]-N,N'-bis(hydroxy-methyl) urea, commonly known as diazolidinyl urea, available under the trade name Germall II® from Sutton Laboratories, Inc.; N,N"-methylenebis{N'-(1-(hydroxymethyl)-2,5-dioxo-4-imidazolidinyl]urea}, commonly known as imidazolidinyl urea, available, e.g., under the trade name Abiol® from 3V-Sigma, Unicide U-13® from Induchem, Germall 115® from Sutton Laboratories, Inc.; polymethoxy bicyclic oxazolidine, available under the trade name Nuosept® C from Hüls America; formaldehyde; glutaraldehyde; polyaminopropyl biguanide; available under the trade name Cosmocil CQ® from ICI Americas, Inc., or under the trade name Mikrokil® from Brooks, Inc; dehydroacetic acid; and mixtures thereof.

(II) ODOR-ABSORBING MATERIAL

The compositions and articles of this invention contain an effective, i.e., odor-absorbing, amount of various odor-absorbing materials. Such materials include, for example, cyclodextrins, zeolites, activated carbon, kieselguhr, chelating agents, chitin,

pH buffered materials, and the like. Especially preferred are cyclodextrins, especially beta-cyclodextrin, and zeolite material having "intermediate" silicate/aluminate ratios (vide infra). Some partially neutralized hydrogel-forming absorbent gelling materials, such as polyacrylate gelling material and acrylate grafted starch gelling material (vide infra), are also useful in the present invention to control certain ammonia-type odors. These materials are discussed with IV. Fluid Absorbent Material because they also function as fluid absorbent materials.

(A). Cyclodextrins

The preferred odor absorbing material is uncomplexed cyclodextrin which can be added to the composition of the present invention. As used herein, the term "cyclodextrin" includes any of the known cyclodextrins such as unsubstituted cyclodextrins containing from six to twelve glucose units, especially, alpha-cyclodextrin, beta-cyclodextrin, gamma-cyclodextrin and/or their derivatives and/or mixtures thereof. The alpha-cyclodextrin consists of six glucose units, the beta-cyclodextrin consists of seven glucose units, and the gamma-cyclodextrin consists of eight glucose units arranged in a donut-shaped ring. The specific coupling and conformation of the glucose units give the cyclodextrins a rigid, conical molecular structure with a hollow interior of a specific volume. The "lining" of the internal cavity is formed by hydrogen atoms and glycosidic bridging oxygen atoms, therefore this surface is fairly hydrophobic. The unique shape and physical-chemical property of the cavity enable the cyclodextrin molecules to absorb (form inclusion complexes with) organic molecules or parts of organic molecules which can fit into the cavity. Many odor molecules can fit into the cavity.

Non-derivatised (normal) beta-cyclodextrin can be used and is preferred. When non-derivatised beta-cyclodextrin is used to prepare the absorbent composition, the aqueous solution is preferably heated. A preferred method is to spray an almost saturated aqueous solution of beta-cyclodextrin, preferably heated, e.g., from about 40°C to about 90°C, preferably from about 50°C to about 80°C, more preferably from about 60°C to about 75°C, onto the absorbent material, preferably with mixing or stirring, to permit a uniform incorporation of as much as possible of the cyclodextrin with the least amount of water.

Another preferred method to apply the beta-cyclodextrin to absorbent material is to spray an aqueous slurry of solid beta-cyclodextrin powder, preferably of small particle size beta-cyclodextrin particles, preferably with mixing or stirring, onto the absorbent material. Beta-Cyclodextrin powder in the slurry typically has an average particle size of less than about 12 microns, preferably less than about 10 microns, more preferably less than about 8 microns, and even more preferably less than about 5 microns, to provide the

best odor control benefit. The particle size is typically between about 0.001 and 10 microns, preferably between about 0.05 and 5 microns. It is highly desirable that at least an effective amount of particles having the said particle sizes. It is desirable that at least about 50%, preferably at least about 65%, more preferably at least about 80%, of the beta-cyclodextrin powder that is present have the said particle sizes.

These small particles of the invention are conveniently prepared by grinding techniques. Cyclodextrin crystals with large particle sizes can be pulverized to obtain the desired smaller particles of less than about 12 microns by using, e.g., a fluid energy mill. In one preferred method, the large beta-cyclodextrin crystals can be pulverized into small particles, then added to water to form the desired slurry. In another preferred method a slurry of large beta-cyclodextrin can be milled to obtain a small particle size slurry. Examples of fluid energy mills are the Trost Air Impact Pulverizers, sold by Garlock Inc., Plastomer Products, Newtown, Pennsylvania; the Micronizer fluid energy mills sold by Sturtevant, Inc., Boston, Massachusetts; and the Spiral Jet Mill sold by Alpine Division, MicroPul Corporation (Hosokawa Micron International, Inc.), Summit, New Jersey.

As used herein, the particle size refers to the largest dimension of the particle and to the ultimate (or primary) particles. The size of these primary particles can be directly determined with optical or scanning electron microscopes. The slides must be carefully prepared so that each contains a representative sample of the bulk cyclodextrin powder. The particles sizes can also be measured by any of the other well-known methods, e.g., wet sieving (non-aqueous), sedimentation, light scattering, etc. A convenient instrument that can be used to determine the particle size distribution of the dry powder directly (without having to make a liquid suspension or dispersion) is the Malvern Particle and Droplet Sizer, Model 2600C, sold by Malvern Instruments, Inc., Southborough, Massachusetts. Some caution should be observed in that some of the dry particles may remain agglomerated. The presence of agglomerates can be further determined by microscopic analysis. Some other suitable methods for particle size analysis are described in the article "Selecting a particle size analyzer: Factors to consider," by Michael Pohl, published in Powder and Bulk Engineering, Volume 4 (1990), pp. 26-29, incorporated herein by reference. It is recognized that the very small particles of the invention can readily aggregate to form loose agglomerates that are easily broken apart by either some mechanical action or by the action of water. Accordingly, particles should be measured after they are broken apart, e.g., by agitation or sonication. The method, of course, should be selected to accommodate the particle size and maintain the

integrity of the complex particles, with iterative measurements being made if the original method selected proves to be inappropriate.

Other cyclodextrins useful in the present invention are highly water-soluble such as, alpha-cyclodextrin and derivatives thereof, gamma-cyclodextrin and derivatives thereof, derivatised beta-cyclodextrins, and/or mixtures thereof. The derivatives of cyclodextrin consist mainly of molecules wherein some of the OH groups are converted to OR groups. Cyclodextrin derivatives include, e.g., those with short chain alkyl groups such as methylated cyclodextrins, and ethylated cyclodextrins, wherein R is a methyl or an ethyl group; those with hydroxyalkyl substituted groups, such as hydroxypropyl cyclodextrins and/or hydroxyethyl cyclodextrins, wherein R is a $-\text{CH}_2\text{-CH}(\text{OH})\text{-CH}_3$ or a $-\text{CH}_2\text{CH}_2\text{-OH}$ group; branched cyclodextrins such as maltose-bonded cyclodextrins; cationic cyclodextrins such as those containing 2-hydroxy-3(dimethylamino)propyl ether, wherein R is $\text{CH}_2\text{-CH}(\text{OH})\text{-CH}_2\text{-N}(\text{CH}_3)_2$ which is cationic at low pH; quaternary ammonium, e.g., 2-hydroxy-3-(trimethylammonio)propyl ether chloride groups, wherein R is $\text{CH}_2\text{-CH}(\text{OH})\text{-CH}_2\text{-N}^+(\text{CH}_3)_3\text{Cl}^-$; anionic cyclodextrins such as carboxymethyl cyclodextrins, cyclodextrin sulfates, and cyclodextrin succinylates; amphoteric cyclodextrins such as carboxymethyl/quaternary ammonium cyclodextrins; cyclodextrins wherein at least one glucopyranose unit has a 3-6-anhydro-cyclomalto structure, e.g., the mono-3-6-anhydrocyclodextrins, as disclosed in "Optimal Performances with Minimal Chemical Modification of Cyclodextrins", F. Diedaini-Pilard and B. Perly, The 7th International Cyclodextrin Symposium Abstracts, April 1994, p. 49, herein incorporated by reference; and mixtures thereof. Other cyclodextrin derivatives are disclosed in U.S. Pat. Nos: 3,426,011, Parmerter et al., issued Feb. 4, 1969; 3,453,257; 3,453,258; 3,453,259; and 3,453,260, all in the names of Parmerter et al., and all issued July 1, 1969; 3,459,731, Gramera et al., issued Aug. 5, 1969; 3,553,191, Parmerter et al., issued Jan. 5, 1971; 3,565,887, Parmerter et al., issued Feb. 23, 1971; 4,535,152, Szejtli et al., issued Aug. 13, 1985; 4,616,008, Hirai et al., issued Oct. 7, 1986; 4,678,598, Ogino et al., issued Jul. 7, 1987; 4,638,058, Brandt et al., issued Jan. 20, 1987; and 4,746,734, Tsuchiyama et al., issued May 24, 1988; all of said patents being incorporated herein by reference.

Highly water-soluble cyclodextrins are those having water solubility of at least about 10 g in 100 ml of water at room temperature, preferably at least about 20 g in 100 ml of water, more preferably at least about 25 g in 100 ml of water at room temperature. These are easy to use, but are typically more expensive than the non-derivatized beta-cyclodextrin. Examples of preferred water-soluble cyclodextrin derivatives suitable for use herein are hydroxypropyl alpha-cyclodextrin, methylated alpha-cyclodextrin,

methylated beta-cyclodextrin, hydroxyethyl beta-cyclodextrin, and hydroxypropyl beta-cyclodextrin. Hydroxyalkyl cyclodextrin derivatives preferably have a degree of substitution of from about 1 to about 14, more preferably from about 1.5 to about 7, wherein the total number of OR groups per cyclodextrin is defined as the degree of substitution. Methylated cyclodextrin derivatives typically have a degree of substitution of from about 1 to about 18, preferably from about 3 to about 16. A known methylated beta-cyclodextrin is heptakis-2,6-di-O-methyl- β -cyclodextrin, commonly known as DIMEB, in which each glucose unit has about 2 methyl groups with a degree of substitution of about 14. A preferred, more commercially available methylated beta-cyclodextrin is a randomly methylated beta-cyclodextrin having a degree of substitution of about 12.6. The preferred cyclodextrins are available, e.g., from Cerestar USA, Inc. and Wacker Chemicals (USA), Inc.

It can be desirable to use a mixture of cyclodextrins. Such mixtures can complex with a wider range of odor molecules having a wider range of molecular sizes. Preferably at least a portion of such a mixture of cyclodextrins is alpha-cyclodextrin or its derivatives, gamma-cyclodextrin or its derivatives thereof, and/or beta-cyclodextrin or its derivatives.

Cyclodextrin molecules are known for their ability to form complexes with perfume ingredients and have typically been taught as a perfume carrier. The prior art teaches the use of drier-added fabric softener sheets containing high levels of cyclodextrin/perfume complexes wherein the fabrics treated with this solid cyclodextrin complex release perfume when the fabrics are rewetted. The art also teaches that cyclodextrin/perfume complexes used in aqueous rinse-added fabric softener compositions must be protected, e.g., with a hydrophobic wax coating so the cyclodextrin/perfume complexes will not decompose due to the presence of water. See U.S. Pat. Nos. 5,102,564 Gardlik et al., issued April 7, 1992; 5,234,610, Gardlik et al., issued August 10, 1993; 5,234,611 Trinh, et al., issued August 10, 1993, all of said patents incorporated herein by reference. Absorbent compositions treated with aqueous compositions of the present invention, which contain low levels of unprotected cyclodextrin/perfume complex, also exhibit perfume release upon rewetting, as discussed hereinafter. This phenomenon provides a benefit in that absorbent compositions treated according to the present invention which contains a small amount of cyclodextrin/perfume complex will thus remain fresh longer, via a perfume release, when said absorbent composition is wetted.

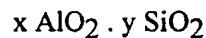
For reducing malodor impression on the absorbent composition herein, the cyclodextrin is preferably applied as a spray. It is preferable that the level of

cyclodextrin is from about 0.01% to about 30%, preferably from about 0.01% to about 25%, more preferably from about 0.5% to about 20%, most preferably from about 1% to about 15%, by weight of the absorbent composition. Absorbent compositions with higher concentrations are more effective, but are not normally economical.

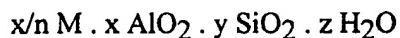
For effective odor control, the absorbent article of the present invention typically contains from about 0.01 g to about 20 g, preferably from about 0.02 g to about 15 g and more preferably from about 0.03 g to about 10 g, of uncomplexed cyclodextrin.

(B). Zeolite Odor-Absorbing Material

In general terms, traditional zeolites comprise an aluminate/ silicate framework, with associated cations, M, providing overall electrical neutrality. Empirically, the zeolite framework can be represented as



and the electrically neutral zeolite as



wherein: x and y are each integers, M is a cation and n is the charge on the cation. As noted by the empirical formula, zeolites may also comprise waters of hydration (z H₂O). M can be a wide variety of cations, e.g., Na⁺, K⁺, NH₄⁺, alkylammonium, heavy metals, and the like.

A preferred class of zeolites useful in the present invention is characterized as "intermediate" silicate/aluminate zeolites. The "intermediate" zeolites are characterized by SiO₂/AlO₂ molar ratios of less than about 10. Typically, the molar ratio of SiO₂/AlO₂ will range from about 2 to about 10. The intermediate zeolites have three advantages over "high" zeolites, disclosed in U.S. Pat. Nos. 4,795,482 and 4,826,497, which are incorporated herein by reference. First, the intermediate zeolites have a higher capacity for amine-type odors which is important for absorbing urine and menses odors. Second, the intermediate zeolites have a larger surface area (about 700-800 m²/g) than high zeolites (about 400 m²/g). Therefore, less intermediate zeolite is needed to absorb a given amount of odor on a weight to weight basis. Third, intermediate zeolites are more moisture tolerant and retain more odor-absorbing capacity in the presence of water.

A wide variety of intermediate zeolites suitable for use herein are commercially available as VALFOR CP301-68, VALFOR 300-63, VALFOR CP300-35 and VALFOR CP300-56, from PQ Corporation, and the CBV100 series (other than Mordenite, as noted below) of zeolites from Conteka.

The zeolites used herein are not of the fibrous type, e.g., various Mordenites, and some types of Y zeolites, since these may be subject to safety issues. Accordingly, the term "zeolite" as used herein is intended to encompass only the nonfibrous zeolites.

While some naturally-occurring zeolites meet the objectives of this invention, the synthetic zeolites of the types available in commerce are generally more preferred.

High zeolites are also preferred and can be employed in the practice of this invention either alone, or in combination with the intermediate ratio zeolites. High zeolites include, for example, the well-known "molecular sieve" zeolites of the ZSM, beta zeolite, etc., type (generally in the 1-10 micron particle size range) and the zeolite materials marketed under the trade name ABSCENTS by the Union Carbide Corporation and UOP. ABSCENTS are typically available as a white powder in the 3-5 micron particle size range (See: ABSCENTS, A New Approach for Odor Control by A. J. Gioffre, copyright 1988 by the Union Carbide Corporation). Such materials are preferred over the "intermediate" zeolites for control of odors associated with sulfur compounds, e.g., thiols, mercaptans.

Various other modified zeolite-type materials which can be used in the present invention, such as the manganese-aluminum-phosphorus-silicon-oxide molecular sieves and other zeolite odor-absorbing compositions are described in U.S. Pat. Nos. 4,793,833, Lok et al.; 4,604,110; 4,437,429; and 4,648,977, which are incorporated herein by reference.

For effective odor control, the absorbent article of the present invention typically contains from about 0.01 g to about 20 g, preferably from about 0.02 g to about 15 g and more preferably from about 0.01 g to about 10 g, of zeolite.

(C). Carbon Odor-Absorbing Material

The carbon material employed herein is the material well known in commercial practice as an adsorbent for organic molecules and/or for air purification purposes. Carbon suitable for use herein is available from a variety of commercial sources under trade names such as CALGON Type "CPG", Type "PCB", Type "SGL", Type "CAL", and Type "OL." Often, such carbon material is referred to simply as "activated" carbon or "activated" charcoal. Typically, it is available in the form of extremely fine, dusty particles (e.g., 0.1-300 microns) having large surface areas (about 200 to several thousand m²/g). It is to be understood that any of the "air purifying" or "activated" carbons of commerce can be used in the practice of this invention.

If the zeolites herein are optionally used in conjunction with the activated carbon, it is preferred (for aesthetics reasons) to coat the carbon with the zeolite using a binder.

Other odor-absorbing materials include kieselguhr, chelating materials, chitin, pH buffered materials, and the like.

(III) OPTIONAL MOISTURE-ACTIVATED PROTECTED PERFUME

Moisture-activated encapsulated perfume includes any encapsulated perfume system which will release the perfume when wetted by water. Preferably, moisture-activated perfume includes cyclodextrin/perfume inclusion complexes, polysaccharide matrix perfume microcapsules, and mixtures thereof. The odor absorbing material and the moisture-activated encapsulated perfume can be present in the fluid-retaining absorbent core or the fluid-receiving front face (topsheet) of these articles.

Cyclodextrin/perfume inclusion complexes are very stable in the dry state. Even the very volatile perfume molecules are bound in the cavity of the cyclodextrin molecules and do not provide perceptible odor. Upon wetting by an aqueous fluid such as a body fluid, the perfume is released to provide a burst of fragrance. A greater variety of perfumes can be used to accommodate a variety of consumer preferences.

In polysaccharide matrix perfume microcapsules, the perfume is dispersed as minute droplets in, e.g., a starch/dextrin solid cellular matrix. Moisture swells and softens the polysaccharide matrix to release the encapsulated perfume.

Preferably, cyclodextrin/perfume inclusion complexes and the polysaccharide matrix perfume microcapsules contain volatile perfume.

The compositions and articles of this invention preferably contain an effective amount of various moisture-activated encapsulated perfume particles. Such materials include, for example, cyclodextrin/perfume inclusion complexes, polysaccharide cellular matrix perfume microcapsules, and the like. Encapsulation of perfume minimizes interaction with, and/or depletion by, odor-absorbing materials before use of the product. Perfume is released when the materials are wetted, to provide a pleasant odor signal in use. Especially preferred are cyclodextrin inclusion complexes of volatile perfumes, with a particle size of less than about 12 microns.

(A). Perfume

The perfumes and compositions of this invention are the conventional ones known in the art. Selection of any perfume component, or amount of perfume, is based on functional and aesthetic considerations. Preferred perfume components useful in the present invention are the highly volatile, and the moderately volatile perfume ingredients, more preferably the highly volatile, low boiling perfumes.

The highly volatile, low boiling, perfume ingredients typically have boiling points of about 260°C or lower, preferably below about 250°C. These highly volatile perfumes are fleeting and are quickly lost as they are released. Many of the more moderately volatile perfume ingredients are also quickly lost. The moderately volatile perfume ingredients are those having boiling points of from about 250°C to about 300°C. Many of the perfume ingredients as discussed hereinafter, along with their odor characters, and their physical and chemical properties, such as boiling point and molecular weight, are given in "Perfume and Flavor Chemicals (Aroma Chemicals)," Steffen Arctander, published by the author, 1969, incorporated herein by reference.

Nonlimiting examples of preferred volatile perfume ingredients are allo-ocimene, allyl caproate, allyl heptoate, amyl acetate, amyl propionate, anethole, anisic aldehyde, anisole, benzaldehyde, benzyl acetate, benzyl acetone, benzyl alcohol, benzyl butyrate, benzyl formate, benzyl iso valerate, benzyl propionate, beta gamma hexenol, camphene, carvacrol, laevo-carveol, d-carvone, laevo-carvone, cinnamyl formate, cis-3-hexenyl tiglate, cis-jasmone, cis-3-hexenyl acetate, citral, citronellal, citronellol, citronellyl acetate, citronellyl isobutyrate, citronellyl nitrile, citronellyl propionate, cyclohexyl ethyl acetate, para-cymene, cuminic alcohol, cuminic aldehyde, Cyclal C, decyl aldehyde, dihydrolinalool, dihydro myrcenol, dihydromyrcenyl acetate, dimethyl benzyl carbinol, dimethyl benzyl carbonyl acetate, dimethyl phenyl carbinol, dimethyl octanol, ethyl acetate, ethyl aceto acetate, ethyl amyl ketone, ethyl butyrate, ethyl hexyl ketone, ethyl phenyl acetate, eucalyptol, fenchyl acetate, fenchyl alcohol, Flor acetate (tricyclo decenyl acetate), frutene (tricyclo decenyl propionate), gamma methyl ionone, gamma-nonalactone, geranial, geraniol, geranyl acetate, geranyl formate, geranyl isobutyrate, geranyl nitrile, hexenol, cis-3-hexenyl acetate, hexenyl isobutyrate, hexyl acetate, hexyl formate, hexyl neopentanoate, hexyl tiglate, hydratropic alcohol, hydroxycitronellal, alpha-ionone, beta-ionone, gamma-ionone, alpha-irone, isoamyl alcohol, isobornyl acetate, isobutyl benzoate, isononyl acetate, isononyl alcohol, isomenthol, isomenthone, para-isopropyl phenylacetaldehyde, isopulegol, isopulegyl acetate, isoquinoline, lauric aldehyde (dodecanal), Ligustral, d-limonene, linalool, linalool oxide, linalyl acetate, linalyl formate, linalyl propionate, menthone, iso-menthone, menthyl acetate, methyl

acetophenone, methyl amyl ketone, methyl anthranilate, methyl benzoate, methyl benzyl acetate, methyl chavicol, methyl eugenol, methyl heptenone, methyl heptine carbonate, methyl heptyl ketone, methyl hexyl ketone, methyl nonyl acetaldehyde, methyl nonyl ketone, methyl phenyl carbonyl acetate, alpha-iso "gamma" methyl ionone, methyl octyl acetaldehyde, myrcene, myrcenyl acetate, myrcenol, nerol, nerol, neryl acetate, nonyl acetate, nonyl aldehyde, octalactone, octyl alcohol (octanol-2), octyl aldehyde, para-cymene, para-methyl acetophenone, phenyl acetaldehyde, phenyl ethyl acetate, phenyl ethyl alcohol, phenyl ethyl dimethyl carbinol, phenoxy ethanol, alpha pinene, beta-pinene, prenyl acetate, propyl butyrate, pulegone, rose oxide, safrole, gamma-terpinene, 4-terpinenol, alpha-terpineol, terpinolene, terpinyl acetate, tetrahydro linalool, tetrahydro myrcenol, tonalid, undecenal, Veratrol, Verdox, vertenex, Viridine. Some natural oils also contain large percentages of highly volatile perfume ingredients and are useful in the perfume compositions of the present invention, for example, lavandin contains as major components: linalool, linalyl acetate, geraniol and citronellol, and lemon oil and orange terpenes both contain about 95% d-limonene.

Examples of moderately volatile perfume ingredients which can be used in perfume compositions of this invention are amyl cinnamic aldehyde, iso-amyl salicylate, diphenyl methane, gamma-n-methyl ionone, isobutyl quinoline, indole, beta-caryophyllene, cedrene, cinnamic alcohol, dimethyl benzyl carbonyl acetate, eugenol, flor acetate, heliotropine, 3-cis-hexenyl salicylate, hexyl salicylate, lilial (para-tertiary-butyl-alpha-methyl hydrocinnamic aldehyde), gamma-methyl ionone, nerolidol, patchouli alcohol, methyl-n-methyl anthranilate, dodecalactone, lilial (p-t-bucinal), phenyl heptanol, phenyl hexanol, ethyl methyl phenyl glycidate, para-methoxy acetophenone, amyl benzoate, phenoxy ethyl propionate and veratraldehyde.

The odor detection threshold of an odorous material is the lowest vapor concentration of that material which can be olfactorily detected. The odor detection threshold and some odor detection threshold values are discussed in, e.g., "Standardized Human Olfactory Thresholds", M. Devos et al, IRL Press at Oxford University Press, 1990, and "Compilation of Odor and Taste Threshold Values Data", F. A. Fazzalari, editor, ASTM Data Series DS 48A, American Society for Testing and Materials, 1978, both of said publications being incorporated by reference. The use of small amounts of perfume ingredients that have low odor detection threshold values can improve perfume odor character, even though they are not as volatile as perfume ingredients of group (a) which are given hereinabove.. Perfume ingredients having significantly low detection threshold, useful in the absorbent article of the present invention, are selected from the group consisting of coumarin, vanillin, ethyl vanillin, methyl dihydro isoasmonate,

isoeugenol, lyral, gamma-undecalactone, gamma-dodecalactone, methyl beta naphthyl ketone, and mixtures thereof.

(B). Formation of Cyclodextrin/Perfume Inclusion Complexes

The perfume/cyclodextrin inclusion complexes of this invention are formed in any of the ways known in the art. Typically, the complexes are formed either by bringing the perfume and the cyclodextrin together in a suitable solvent, e.g., water, or, preferably, by kneading/slurrying the ingredients together in the presence of a suitable, preferably minimal, amount of solvent, preferably water. The kneading/slurrying method is particularly desirable because it produces smaller complex particles and requires the use of less solvent, eliminating or reducing the need to further reduce particle size and separate excess solvent. Disclosures of complex formation can be found in Atwood, J.L., J.E.D. Davies & D.D. MacNichol, (Ed.): Inclusion Compounds, Vol. III, Academic Press (1984), especially Chapter 11, Atwood, J.L. and J.E.D. Davies (Ed.): Proceedings of the Second International Symposium of Cyclodextrins Tokyo, Japan, (July, 1984), and J. Szejtli, Cyclodextrin Technology, Kluwer Academic Publishers (1988), said publications incorporated herein by reference.

In general, perfume/cyclodextrin complexes have a molar ratio of perfume compound to cyclodextrin of about 1:1. However, the molar ratio can be either higher or lower, depending on the size of the perfume compound and the identity of the cyclodextrin compound. The molar ratio can be determined by forming a saturated solution of the cyclodextrin and adding the perfume to form the complex. In general the complex will precipitate readily. If not, the complex can usually be precipitated by the addition of electrolyte, change of pH, cooling, etc. The complex can then be analyzed to determine the ratio of perfume to cyclodextrin.

As stated hereinbefore, the actual complexes are determined by the size of the cavity in the cyclodextrin and the size of the perfume molecule. Desirable complexes can be formed using mixtures of cyclodextrins since perfumes are normally mixtures of materials that vary widely in size. It is usually desirable that at least a majority of the material be alpha-, beta-, and/or gamma-cyclodextrin, more preferably beta-cyclodextrin. The content of the perfume in the beta-cyclodextrin complex is typically from about 5% to about 15%, more normally from about 7% to about 12%.

Continuous complexation operation usually involves the use of supersaturated solutions, kneading/slurrying method, and/or temperature manipulation, e.g., heating and then either cooling, freeze-drying, etc. The complexes are dried to a dry powder to make the desired composition. In general, the fewest possible process steps are preferred to avoid loss of perfume.

(C). Complex Particle Size

Complexes of this invention having a particle size of less than about 12 microns, preferably less than about 10 microns, more preferably less than about 8 microns, and even more preferably less than about 5 microns, improve the release, especially the speed of release of the perfume when the complexes are wetted.

The particle size is typically between about 0.001 and 10 microns, preferably between about 0.05 and 5 microns. It is highly desirable that at least an effective amount of the perfume be in complexes having the said particle sizes. It is desirable that at least about 75%, preferably at least about 80%, more preferably at least about 90%, and even more preferably at least about 100%, of the complex that is present have the said particle sizes. Methods for determining particle sizes have been given hereinbefore.

These small particles of the invention are conveniently prepared by kneading methods and/or grinding techniques. Cyclodextrin complexes with large particle sizes can be pulverized to obtain the desired smaller particles of less than about 12 microns by using, e.g., a fluid energy mill. Examples of fluid energy mills are the Trost Air Impact Pulverizers, sold by Garlock Inc., Plastomer Products, Newtown, Pennsylvania; the Micronizer fluid energy mills sold by Sturtevant, Inc., Boston, Massachusetts; and the Spiral Jet Mill sold by Alpine Division, MicroPul Corporation (Hosokawa Micron International, Inc.), Summit, New Jersey.

It is highly desirable that at least an effective amount of the cyclodextrin/perfume complex be applied to the article. Effective amounts are typically in the range of from about 0.005 g to about 10 g, preferably from about 0.01 g to about 3 g, more preferably from about 0.02 g to about 1 g per article.

(D). Matrix Perfume Microcapsules

Water-soluble cellular matrix perfume microcapsules are solid particles containing perfume stably held in the cells. The water-soluble matrix material comprises mainly polysaccharide and polyhydroxy compounds. The polysaccharides are preferably higher polysaccharides of the non-sweet, colloidally-soluble types, such as natural gums, e.g., gum arabic, starch derivatives, dextrinized and hydrolyzed starches, and the like. The polyhydroxy compounds are preferably alcohols, plant-type sugars, lactones, monoethers, and acetals. The cellular matrix microcapsules useful in the present invention are prepared by, e.g., (1) forming an aqueous phase of the polysaccharide and polyhydroxy compound in proper proportions, with added emulsifier if necessary or desirable; (2) emulsifying the perfumes in the aqueous phase; and (3) removing moisture while the mass is plastic or flowable, e.g., by spray drying droplets of the emulsion. The

matrix materials and process details are disclosed in, e.g., U.S. Pat. No. 3,971,852, Brenner et al., issued July 27, 1976, which is incorporated herein by reference.

The present invention preferably has minimal non-encapsulated surface perfume, preferably less than about 1%.

Moisture-activated perfume microcapsules can be obtained commercially, e.g., as IN-CAPR from Polak's Frutal Works, Inc., Middletown, New York; and as Optilok System® encapsulated perfumes from Encapsulated Technology, Inc., Nyack, New York.

Water-soluble matrix perfume microcapsules preferably have size of from about 0.5 micron to about 300 microns, more preferably from about 1 micron to about 200 microns, most preferably from about 2 microns to about 100 microns.

It is essential that at least an effective amount of the water-activated matrix perfume microcapsules be applied to the article. Effective amounts are typically in the range of from about 0.001 g to about 5 g, preferably from about 0.005 g to about 1 g, more preferably from about 0.01 g to about 0.5 g, per article.

The moisture-activated encapsulated perfume (III) does not interfere with the efficacy of the odor absorbing material (II).

(E). Incorporation of Encapsulated Perfume into Absorbent Articles

Small particle size cyclodextrin/perfume complexes can be applied to the fluid absorbent articles by uniformly sprinkling, mixing, or distributing the cyclodextrin/perfume complex powder onto the fluid absorbent materials.

However, it is commonly known that when in use, the body fluid is not normally distributed to the whole fluid absorbent article, e.g., diaper, but usually localized in a portion of the article. Actually, modern disposable diapers are designed with a concentration of the fluid absorbent materials at different locations depending on the sex of the wearers. Similarly, it is not necessary to apply the cyclodextrin/perfume complex powder to the entire fluid absorbent article. Preferably, cyclodextrin/perfume complex powder is applied to areas most likely to be wetted by body fluids to avoid waste in the areas which do not normally receive the body fluids.

Furthermore, when distributed as a dry powder, the cyclodextrin/perfume complex particles may shift away from the preferred locations, and move to the areas where they have less chance to be solubilized by the body fluids, and become less effective. The shifting happens both during the manufacturing processes, e.g., folding, and packaging of the articles, and during later steps, e.g., transportation, and unfolding and refolding of the fluid absorbent article in use. Therefore, it is preferred to provide a means to immobilize

the cyclodextrin/perfume complex powder on the preferred locations in the fluid absorbent articles.

Immobilization can be accomplished by a variety of methods, i.e., hot-melt adhesives, thermoplastic binder fibers, thermoplastic binder particles, or other methods known to those skilled in the art.

A preferred method is to use a water-soluble binder to attach the cyclodextrin/perfume complex powder to the fluid absorbent core and/or topsheets. The water-soluble binders are preferably polymeric. They can be low melting polymers such as polyethylene glycols (PEG), poly(ethylene glycol) methyl ethers, or mixtures thereof. Preferred low melting water-soluble PEG materials have the general formula RO-(CH₂CH₂O)_n-R wherein each R is a hydrogen radical, a C₁-C₄ alkyl radical, or mixtures of such radicals, and have an average molecular weight (MW) of from about 600 to about 20,000 (n is from about 13 to about 450). More preferred PEG materials are polyethylene glycols, poly(ethylene glycol) methyl ethers, or mixtures thereof, with MW of from about 1,000 to about 9,000 (n from about 20 to about 200), more preferably from about 1,400 to about 4,500 (n from about 30 to about 100). The weight ratio of the cyclodextrin/perfume complex to the PEG material is from about 3:1 to about 1:5, preferably from about 2:1 to about 1:3.

A preferred process of attaching cyclodextrin/perfume complex powder involves admixing solid small-particle-sized cyclodextrin/perfume complex powder with a molten hydrophilic PEG material. The molten mixture can be sprayed directly to the dry fluid absorbent materials or topsheets, then letting the droplets solidify on said materials or nonwoven topsheets. Another preferred method is to pulverize the solidified cyclodextrin complex/binder mixture into small particles first. Said particles can then be attached and immobilized to the surface of the fluid absorbent materials or the nonwoven topsheets by distributing the particles on said surface, melting said particles by, e.g., a heat source, and then resolidifying to bind said particles to said surface. At the cyclodextrin/perfume complex to the PEG material weight ratio of from about 3:1 to about 1:3, the molten mixture can be solidified to room temperature then pulverized at room temperature or cryogenically. At the cyclodextrin/perfume complex to the PEG material weight ratio of from about 1:2 to about 1:5, the molten mixture can be prilled by, e.g., spray drying, marumarizing, etc., into solid prills. The solid cyclodextrin/perfume complex/PEG material mixture particles preferably have sizes of from about 10 microns to about 1,000 microns, more preferably from about 20 microns to about 600 microns.

Another preferred method is to apply the cyclodextrin/perfume complex slurry to the fluid absorbent material and/or nonwoven topsheet. Upon drying, the small particles of the cyclodextrin complex adhere to the absorbent material and are immobilized on said material. This can be done, e.g., by spraying the cyclodextrin/perfume complex slurry onto the already formed and dry absorbent fiber web.

It is also preferred to incorporate a water-soluble polymer, such as PEG, polyvinyl alcohols, polyacrylic acids, and polyvinylpyrrolidone into the aqueous cyclodextrin/perfume complex slurry after the complex has been formed. The aqueous mixture is distributed, e.g., by spraying, to the fluid absorbent materials or the nonwoven topsheets, then the resulting combination is dried, and thus attaching the cyclodextrin to said fluid absorbent materials or topsheets. Preferred MW of said polymers are from about 1,000 to about 200,000; more preferred are from about 2,000 to about 100,000.

(IV) FLUID ABSORBENT MATERIAL

Fluid absorbent material can be any material which is generally compressible, conformable, non-irritating to the wearer's skin, and which is capable of absorbing and retaining fluids.

The fluid absorbent material can be constructed from any of a variety of materials commonly used in disposable absorbent articles. These materials are described in U.S. Pat. Nos.: 3,905,863, Ayers, issued Sept. 16, 1975; 3,974,025, Ayers, issued Aug. 10, 1976; 4,191,609, Trokhan, issued Mar. 4, 1980; 4,440,597, Wells et al., issued Apr. 3, 1984; 4,529,480, Trokhan, issued July 16, 1985; and 4,637,859, Trokhan, issued Jan. 20, 1987, all of said patents incorporated herein by reference. Examples of suitable absorbent materials include creped cellulose wadding, cotton fluff, and citric acid cross-linked cellulose pulp disclosed in U.S. Pat. Nos.: 5,190,563, issued Mar. 2, 1993, 5,183,707, issued Feb. 2, 1993; and 5,137,537, issued Aug. 11, 1992, all issued to Herron et al.; synthetic fibers disclosed in U.S. Pat. No. 4,578,414, Sawyer, issued Mar. 25, 1986; absorbent foams, absorbent sponges, superabsorbent composites, superabsorbent foam, and super absorbent polymers. A preferred fluid absorbent material is comminuted and airlaid wood pulp fibers commonly referred to as absorbent fluff. An absorbent fluff having a density of from about 0.05 g to about 0.175 g per cm³ is generally acceptable.

More preferred fluid absorbent materials are the absorbent gelling materials. As is well known in the art, fluid absorbent gelling materials (sometimes referred to as "AGM" or "super-sorbers") are broadly used in fluid absorbent articles. In general, such AGM's have been used only for their fluid-absorbing properties. Such materials form hydrogels on contact with water (e.g., with urine, blood, and the like). One highly preferred type of hydrogel-forming, absorbent gelling material is based on the hydrolyzed polyacids,

especially neutralized polyacrylic acid. Hydrogel-forming polymeric materials of this type are those which, upon contact with fluids (i.e., liquids) such as water or body fluids, imbibe such fluids and thereby form hydrogels. In this manner, fluid discharged into the fluid absorbent structures herein can be acquired and held. These preferred fluid absorbent gelling materials will generally comprise substantially water-insoluble, slightly cross-linked, partially neutralized, hydrogel-forming polymer materials prepared from polymerizable, unsaturated, acid-containing monomers. In such materials, the polymeric component formed from unsaturated, acid-containing monomers may comprise the entire gelling agent or may be grafted onto other types of polymer moieties such as starch or cellulose. The hydrolyzed polyacrylic acid grafted starch materials are of this latter type. Thus the preferred fluid absorbent gelling materials include hydrolyzed polyacrylonitrile grafted starch, hydrolyzed polyacrylate grafted starch, polyacrylates, maleic anhydride-isobutylene copolymers and combinations thereof. Especially preferred fluid absorbent gelling materials are the hydrolyzed polyacrylates and hydrolyzed polyacrylate grafted starch.

Whatever the nature of the polymer components of the preferred fluid absorbent gelling materials, such materials will in general be slightly cross-linked. Cross-linking serves to render these preferred hydrogel-forming absorbent materials substantially water-insoluble, and cross-linking also in part determines the gel volume and extractable polymer characteristics of the hydrogels formed therefrom. Suitable cross-linking agents are well known in the art and include, for example: (1) compounds having at least two polymerizable double bonds; (2) compounds having at least one polymerizable double bond and at least one functional group reactive with the acid-containing monomer material; (3) compounds having at least two functional groups reactive with the acid-containing monomer material; and (4) polyvalent metal compounds which can form ionic cross-linkages. Cross-linking agents of the foregoing types are described in greater detail in U.S. Pat. No. 4,076,663, Masuda et al., issued Feb. 28, 1978. Preferred cross-linking agents are the di- or polyesters of unsaturated mono- or polycarboxylic acids with polyols, the bisacrylamides and the di- or triallyl amines. Especially preferred cross-linking agents are N,N'-methylenebisacrylamide, trimethylol propane triacrylate and triallyl amine. The cross-linking agent will generally comprise from about 0.001 mole percent to about 5 mole percent of the preferred materials. More preferably, the cross-linking agent will comprise from about 0.01 mole percent to about 3 mole percent of the absorbent gelling materials used herein.

The preferred, slightly cross-linked, hydrogel-forming absorbent gelling materials will generally be employed in their partially neutralized form. For purposes described

herein, such materials are considered partially neutralized when at least about 25 mole percent, preferably at least about 50 mole percent, and more preferably at least about 75 mole percent, of monomers used to form the polymer are acid group-containing monomers which have been neutralized with a salt-forming cation. Suitable salt-forming cations include alkali metal, ammonium, substituted ammonium and amines. This percentage of the total monomers utilized which are neutralized acid group-containing monomers is referred to as the "degree of neutralization." Typically, commercial fluid absorbent gelling materials have a degree of neutralization somewhat less than about 90%.

The preferred fluid absorbent gelling materials used herein are those which have a relatively high capacity for imbibing fluids encountered in the fluid absorbent articles; this capacity can be quantified by referencing the "gel volume" of said fluid absorbent gelling materials. Gel volume can be defined in terms of the amount of synthetic urine absorbed by any given fluid absorbent gelling agent buffer and is specified as grams of synthetic urine per gram of gelling agent.

Gel volume in synthetic urine (see Brandt et al., below) can be determined by forming a suspension of about 0.1-0.2 parts of dried fluid absorbent gelling material to be tested with about 20 parts of synthetic urine. This suspension is maintained at ambient temperature under gentle stirring for about 1 hour so that swelling equilibrium is attained. The gel volume (grams of synthetic urine per gram of fluid absorbent gelling material) is then calculated from the weight fraction of the gelling agent in the suspension and the ratio of the liquid volume excluded from the formed hydrogel to the total volume of the suspension. The preferred fluid absorbent gelling materials useful in this invention will have a gel volume of from about 20 to 70 grams, more preferably from about 30 to 60 grams, of synthetic urine per gram of absorbent gelling material.

Another feature of the most highly preferred fluid absorbent gelling materials relates to the level of extractable polymer material present in said materials. Extractable polymer levels can be determined by: (1) contacting a sample of preferred fluid absorbent gelling material with a synthetic urine solution for a substantial period of time (e.g., at least 16 hours) to reach extraction equilibrium; (2) filtering the formed hydrogel from the supernatant liquid; and (3) determining the polymer content of the filtrate. The particular procedure used to determine extractable polymer content of the preferred fluid absorbent gelling agent buffers herein is set forth in U.S. Pat. No. 4,654,039, Brandt, Goldman and Inglin, issued Mar. 31, 1987, Reissue No. 32,649. The fluid absorbent gelling materials which are especially useful in the fluid absorbent articles herein are those which have an equilibrium extractables content in synthetic urine of no more than

about 17%, preferably no more than about 10% by weight of the fluid absorbent gelling material.

The fluid absorbent gelling materials hereinbefore described are typically used in the form of discrete particles. Such fluid absorbent gelling materials can be of any desired shape, e.g., spherical or semi-spherical, cubic, rod-like polyhedral, etc. Shapes having a large greatest dimension/smallest dimension ratio, like needles and flakes, are also contemplated for use herein. Agglomerates of fluid absorbent gelling material particles may also be used.

The size of the fluid absorbent gelling material particles may vary over a wide range. For reasons of industrial hygiene, average particle sizes smaller than about 30 microns are less desirable. Particles having a smallest dimension larger than about 2 mm may also cause a feeling of grittiness in the absorbent article, which is undesirable from a consumer aesthetics standpoint. Furthermore, rate of fluid absorption can be affected by particle size. Larger particles have very much reduced rates of absorption. Fluid absorbent gelling material particles preferably have a particle size of from about 30 microns to about 2 mm for substantially all of the particles. "Particle Size" as used herein means the weighted average of the smallest dimension of the individual particles.

The amount of fluid absorbent gelling material particles used in fluid absorbent cores will depend upon the degree of fluid absorbent capacity desired, and will generally comprise from about 2% to about 50% by weight of the fluid absorbent core, more typically from about 5% to about 20% by weight of the fluid absorbent core.

When fluid absorbent gelling material particles are to be used in the cores of the fluid absorbent articles herein, such cores can be prepared by any process or technique which provides a web comprising a combination of the fibers and the gelling material particles. For example, web cores can be formed by air-laying a substantially dry mixture of hydrophilic fibers and fluid absorbent gelling material particles and, if desired or necessary, by densifying the resulting web. Such a procedure is described more fully in U.S. Pat. No. 4,610,678, Weisman and Goldman, issued Sept. 9, 1986. As indicated in this U.S. Pat. No. 4,610,678, the air-laid webs formed by such a procedure will preferably comprise substantially unbonded fibers and will preferably have a moisture content of about 10% or less.

Another example combining the fibers and the gelling material particles is a tissue laminate. Such a fluid absorbent core is described more fully in U.S. Pat. Nos: 4,950,264, Osborn, issued Aug. 21, 1990; 5,009,653, Osborn, issued Apr. 23, 1991; WO 93/01785, Osborn et al., published Feb. 4, 1993, "Stretchable Absorbent Articles;" and WO 93/01781, Johnson et al., published Feb. 4, 1993, "Curving Shaped Absorbent

Articles," all of said patents incorporated herein by reference. As indicated in these references, glue is applied to an air-laid, latex-bonded tissue and absorbent gelling material is added and then the tissue is folded over.

The density of the fluid absorbent cores which comprise webs of hydrophilic fibers and fluid absorbent gelling material particles can be of importance in determining the fluid absorbent properties of the cores and of the fluid absorbent articles in which such cores are employed. The density of such fluid absorbent cores herein will preferably be in the range of from about 0.06 to about 0.3 g/cm³, and more preferably within the range of from about 0.09 to about 0.22 g/cm³. Typically the basis weight of the fluid absorbent cores herein can range from about 0.02 to 0.12 g/cm².

Density values for cores of this type can be calculated from basis weight and caliper. Caliper is measured under a confining pressure of 0.137 psi (0.94 kPa). Density and basis weight values include the weight of the fluid absorbent gelling materials and the odor-control material. Density of the cores herein need not be uniform throughout the core. Within the density ranges set forth above, the cores can contain regions or zones of relatively higher or relatively lower density.

The size of the fluid absorbent element is dictated by the exact product design selected.

(V) FRONT-FACE MATERIAL (TOPSHEET MATERIAL)

The finished articles herein will typically be provided with a fluid-receiving facing material. The front-face ("topsheet") material used herein can be any compliant, soft-feeling, non-irritating (to the wearer's skin) planar material. It functions to contact the wearer's skin, to receive fluid discharges, to allow the discharges to pass readily therethrough into the absorbent element, and to isolate the wearer's skin from the fluids in the absorbent element.

The topsheet can be porous paper made from natural or synthetic fibers or mixtures thereof, non-woven fabric made from natural or synthetic fibers or mixtures thereof, apertured plastic film, porous foam, or the like.

A preferred topsheet is spun bonded non-woven polyester fabric made from fibers of from about 2.2 to about 2.5 denier, having a basis weight of about 17 g per square meter (m²). Another preferred topsheet material has a basis weight of 22 g per m² and comprises about 65% by weight staple length, 1.5 denier polyester fibers (such as Kodel type 411 polyester fibers as sold by Tennessee Eastman Corporation, Kingsport, Tennessee); about 15% crimped, staple length 1.5 denier rayon fibers; and about 20% acrylic copolymer binder (such as Celanese CPE 8335 as sold by Celanese Corporation,

Charlotte, North Carolina). "Staple length" refers to fibers having a length of at least about 15 mm.

Still another preferred topsheet is constructed from polypropylene fibers which have been carded and thermally bonded in a spaced-apart pattern. Fibers about 3.8 cm long and of from about 1.5 to about 3.0 denier are suitable. A preferred topsheet of this type has a basis weight of about 24 g per m².

Suitable topsheets can also be constructed from apertured plastic films such as those described in U.S. Pat. Nos.: 4,342,314, Radel and Thompson, issued Aug. 3, 1982; 4,341,217, Ferguson and Landrigan, issued July 27, 1982; 4,324,246, Mullane and Smith, issued April 13, 1982; and 3,929,135, Thompson, issued Dec. 30, 1975, all of these patents being incorporated herein by reference.

For example, according to the process of U.S. Pat. No. 4,324,246, supra, a sample of thermoplastic material such as 0.0038 cm thick polyethylene film is heated above its softening point. (The softening point is the temperature at which the thermoplastic material can be formed or molded and is less than the melting point of the material.) The heated thermoplastic material in sheet form is then brought into contact with a heated forming screen. The forming screen is preferably an apertured wire mesh screen having the desired aperture size, pattern and configuration. A vacuum is used to draw the heated film against the forming screen, thereby forming the film into the desired pattern and having the desired hole sizes. While the vacuum is still being applied to the film, a jet of hot air is passed over the film. The hot air jet perforates the film in a pattern corresponding to the pattern and size of apertures in the forming screen.

Fluid-permeable sheets prepared in the manner of U.S. Pat. No. 4,324,246, supra, are conveniently referred to as "formed films." The caliper of such films is important since, if the caliper is too great, liquid may accumulate in the apertures and not readily pass therethrough. For the manufacture of fluid absorbent articles such as diapers, catamenials, incontinence articles, and the like, the sheets typically have a caliper of less than about 0.075 cm, or preferably less than about 0.064 cm.

Another formed-film sheet material useful herein is the resilient, 3-dimensional web exhibiting a fiber-like appearance and tactile impression, comprising a fluid-impervious plastic material, with said web having a multiplicity of apertures, the apertures being defined by a multiplicity of intersecting fiber-like elements, all as disclosed in U.S. Pat. No. 4,342,314, supra. The Radel and Thompson sheet materials can be prepared using hydrophobic plastics such as polyethylene, polypropylene, PVC, and the like, and are well-known for use in fluid absorbent products such as catamenials, and the like.

Yet another type of sheet material useful herein is described in U.S. Pat. No. 3,929,135, supra, and consists of hydrophobic polymer films having holes which are in the form of tapered capillaries. These "tapered capillary" sheets are also known for use in fluid absorbent articles, including adult incontinence articles. They may be prepared from various hydrophobic polymers, as mentioned hereinabove; typically, low density polyethylene having thickness of from 0.0025 to 0.0051 cm is employed.

Reference to U.S. Pat. No. 3,929,135, supra, can be made in order to further visualize tapered capillary sheets. In use, the apices of the capillaries in such tapered capillary topsheets are in contact with the underlying fluid absorbent core material. Generally, tapered capillaries are in the form of a frustum of a conical surface, but it is to be understood that any generally tapered structure, such as a frustum of a pyramid or the like with a triangular, square, or polygonal base, is within the term "tapered capillary"; circular tapered capillaries, however, are used in this description for convenience. It is also to be understood that the tapered capillaries can be asymmetric (i.e., the angle of taper on one side can be different from that on another side) and that the angle of taper can change continuously (i.e., be curved) over the distance from base to apex. In the latter case, the angle of taper is defined as the angle of the tangent to the side of the capillary at its point of minimum apex opening dimension. The angle of taper suitable for use in topsheets according to the practice of this invention is from about 10° to about 60°.

Base opening dimension of the capillaries is defined as the maximum open measurement in the plane of topsheet at said tapered capillary. Apex opening dimension is defined as the maximum open measurement in the apex of said tapered capillary, which apex is remote from the plane of the topsheet. When the tapered capillary is in the form of a frustum of a conical surface, the base and apex opening dimensions are, respectively, the base diameter and the apex diameter. Base diameter and apex diameter are hereinafter used interchangeably with, respectively, base opening dimension and apex opening dimension.

The tapered capillary apex diameter is a diameter which will allow liquid to readily pass from the surface of the topsheet to the underlying fluid absorbent core. The apex diameter is from about 0.004 to about 0.100 inch (0.010 to 0.254 centimeter), preferably from about 0.005 to about 0.020 inch (0.013 to 0.051 centimeter).

The tapered capillary base diameter is selected to satisfy two criteria. The first of these is the subjective feel of the surface of the topsheet which contacts the skin of the user. It has been discovered that polyethylene can be made to exhibit pleasing, clothlike, non-waxy attributes when the base diameter is within the range from about 0.006 to

about 0.250 inch (0.015 to 0.635 centimeter). Preferably, the base diameter should be within the range of from about 0.030 to about 0.060 inch (0.076 to 0.152 centimeter). The second criterion is that the capillary base diameter be small enough to allow an expected liquid droplet to bridge across at least one capillary. This criterion is satisfied by the above dimensions for disposable diapers and sanitary items.

The height of the tapered capillary is defined as the distance between the outermost surface of the topsheet (i.e., that surface which normally contacts the skin of the user) and the apex of the tapered capillary. This height, of course, depends upon apex diameter, base diameter, and angle of taper which have been selected as hereinbefore described. The height of the tapered capillary should provide a structure with a minimum tendency to collapse in use. The characteristics of the material of construction of the topsheet in large measure determine suitable ranges for the height. When the topsheet is low density polyethylene of from 0.001 to 0.002 inch (0.003 to 0.005 cm) thickness and apex diameter and base diameter are in the preferred range, and angle of taper α is in its critical range, the height of the tapered capillary can be from about 0.003 to about 0.159 inch (0.008 to 0.404 centimeter).

A state of relative dryness on the surface of the topsheet implies that most of the liquid which contacts the topsheet is transferred through it to the fluid absorbent element. This in turn implies that each isolated droplet of fluid in contact with the topsheet must be in contact with the base diameter of a tapered capillary. This state of affairs can best be achieved if the land area (the area of the topsheet that exists between the bases of the tapered capillaries) is maintained at a minimum. The minimum limiting value is the case where conical tapered capillaries or pyramidal tapered capillaries are provided in close packed array (where the periphery of the base of each capillary is in contact on all sides with the periphery of the base of adjacent capillaries). The preferred arrangement of minimum land area tends to insure that an individual droplet will contact at least one tapered capillary. A preferred arrangement in disposable diapers is where the tapered capillaries as hereinbefore described are in ordered arrangement with from about 30 to about 1500 tapered capillaries per square inch of topsheet (5 to 231 per square centimeter).

U.S. Pat. No. 4,629,643, Curro and Linman, issued Dec. 16, 1986, discloses a microapertured polymeric film with improved tactile impression, which can also be used in the practice of this invention.

A highly-preferred fluid-permeable formed-film sheet material which can be employed in the practice of this invention is disclosed in U.S. Pat. No. 4,463,045, Ahr et

al., issued July 31, 1984, and reference can be made to that patent to further assist visualization of the Ahr et al. structures.

In general terms, the sheets provided by U.S. Pat. No. 4,463,045, supra, are designed not only to provide a desirable cloth-like tactile impression, but also to substantially eliminate surface gloss. Thus, sheets made of plastic do not have an undesirably shiny, "plasticky" appearance.

"One-way" sheets whose back faces are treated with hydrophilic latex are described in U.S. Pat. No. 4,735,843, Noda, issued April 5, 1988, and these can also be employed herein.

In addition to the sophisticated apertured materials mentioned hereinabove, the practice of the present invention may also be undertaken with hydrophobic sheet materials having simple holes punched therethrough.

It will be understood from the foregoing that the aforesaid, preferred, "sheet" or "film" materials used in the practice of this invention are substantially different from fibrous nonwoven materials, which are characterized by a large number of fibers which overlap each other throughout the thickness of the material. Moreover, such sheet materials are made from materials (preferably, hydrophobic thermoplastic polymeric materials) which provide a clean-appearing, stain-resistant or "non-staining" surface, in use.

Other topsheet materials which can be used herein include, for example, various nonabsorbent fibrous or filamentous network sheets which are aqueous-fluid-permeable by virtue of a multiplicity of holes or channels passing therethrough. Such sheet materials can be prepared by methods well-described in the patent literature. For example, according to the process of U.S. Pat. No. 4,636,419, Madsen et al., issued Jan. 13, 1987, sheets comprising a network of ribboned filaments of two dissimilar chemical types, and with two dissimilar melting or softening points, are contacted and cooled to allow the formation of a network sheet characterized by said different transverse and longitudinal polymer materials. Such sheets can be used in the practice of this invention.

Another sheet material useful herein is the formaminous net comprising a reticular network of polymeric filaments, said net comprising two arrays of filaments oriented at a displacement angle of about 20-90 degrees. Reference can be made to European Patent Application 0215417, filed Sept. 6, 1986, Sneyd et al., to further assist visualization of this sheet. The aforesaid sheet materials can be prepared using hydrophobic plastics such as polyethylene, polypropylene, PVC, and the like, and are well-known for use in absorbent products such as catamenials, and the like. Such sheet materials typically have

a basis weight of about 0.5-5.0 ounces/yd² (about 0.0016 g/cm² - 0.016 g/cm²), a caliper of 5-25 mils, an open area of about 30-80% and a mesh of 20-40.

The size of topsheet is dictated by the product design and the size of the wearer. It can be ascertained by those skilled in the art.

(VI) BACKING SHEET

One major function of the backing sheet (or backsheet) is to prevent body fluids from escaping from, e.g., disposable diaper or catamenial products, and soiling the wearer's outer garments and other surfaces in contact with said products. Any compliant, non-irritating, planar material which is impermeable to body fluids can be used as backsheet. Suitable materials are described with particularity in the hereinbefore incorporated patents and patent application. A preferred backsheet is formed from polyethylene film having a thickness of from about 0.001 to about 0.5 mm, preferably from about 0.012 to about 0.051 mm.

Flushable or biodegradable backing sheets can also be used, e.g., with pantiliner devices herein.

The size of the backsheet is dictated by the exact product design selected and the size of the intended wearer; it can be readily ascertained by those skilled in the art.

(VII) OPTIONAL RETAINING MEANS

The fluid absorbent structures herein can optionally, but preferably, be provided with means to hold them in place on or near the user's body to allow the structures to perform their intended function. For example, diapers and incontinence garments can be provided with well-known commercially-available tape fasteners. Sanitary napkins can be provided with glue stripes facing outward on their backsheet in well-known fashion. Various pins, clips and fasteners of well-known types can optionally be employed. The retaining means also provide an additional benefit in that they can contain the body fluids in a more enclosed space. As a consequence, the malodor is also contained and more readily absorbed and removed by the odor absorbing materials.

A perfume used in the following examples is as follows:

<u>Volatile Perfume Composition</u>	
<u>Component</u>	<u>Wt.%</u>
Alpha Pinene	5.0
Cedarwood Terpenes	20.0
Dihydro Myrcenol	10.0
Eugenol	5.0
Lavandin	15.0
Lemon Oil CP	10.0
Orange Terpenes	15.0
Phenyl Ethyl Alcohol	<u>20.0</u>
Total	100.0

Following are non-limiting examples of moisture-activated encapsulated perfumes (cyclodextrin/perfume inclusion complexes and matrix perfume microcapsules) that can be incorporated in the articles of this invention.

Complex 1

A mobile slurry is prepared by mixing about 1 kg of beta-cyclodextrin and about 1,000 ml of water in a stainless steel mixing bowl of a KitchenAid mixer using a plastic coated heavy-duty mixing blade. Mixing is continued while about 175 g of the perfume is slowly added. The liquid-like slurry immediately starts to thicken and becomes a creamy paste. Stirring is continued for about 30 minutes. The paste is now dough-like in appearance. About 500 ml of water is added to the paste and blended well. Stirring is then resumed for about an additional 30 minutes. During this time the complex again thickens, although not to the same degree as before the additional water is added. The resulting creamy complex is spread in a thin layer on a tray and allowed to air dry. This produces about 1100 g of granular solid which is ground to a fine power. The complex retains some free perfume and still has a residual perfume odor.

Complex 2

The last traces of water in Complex 1 are removed by freeze drying, after which Complex 1 loses about 1% of its weight. Examination of the complex particles by scanning electron microscopy shows that practically all of the ultimate (primary) particles of the complex have particle sizes less than about 5 microns. The resulting solid is washed with diethyl ether to remove the residual uncomplexed perfume. The last traces of ether are removed in vacuo to give Complex 2 as a white powder which is odorless when dry but produces the fragrance of the perfume when added to water.

Slurry 1

A mobile slurry is prepared by mixing about 600 g of beta-cyclodextrin and 600 ml of water in a stainless steel mixing bowl of a Kitchen Aid® mixer using a plastic coated heavy duty mixing blade. Mixing is continued while about 105 g of the perfume is slowly added. The liquid-like slurry immediately starts to thicken and becomes a creamy paste. Stirring is continued for about 30 minutes. About 1,200 ml of water is slowly added to the slurry with stirring. The stirring continues for about an additional 30 minutes to give a liquid Slurry 1.

Slurry 2

A mobile slurry is prepared similarly to that of Slurry 1, except that the additional 1,200 ml of water contains about 20 g of dissolved polyethylene glycol with molecular weight of about 3,400.

Complex Particles 1

Solid cyclodextrin/perfume complex/polyethylene glycol particles are prepared as follows. One part of Complex 1 is mixed thoroughly with about 1 part of molten polyethylene glycol with an average MW of about 3,400, at about 70°. The composition solidifies upon cooling, and is cryogenically ground with dry ice. The resulting solid cyclodextrin/perfume complex/polyethylene glycol particles are sorted to get particle size of less than about 500 microns.

Complex Particles 2

Solid cyclodextrin/perfume complex/polyethylene glycol particles are prepared as follows. One part of Complex 1 is mixed thoroughly with about 3 parts of molten polyethylene glycol with an average MW of about 1,450, at about 80°. The molten composition is atomized in a spray drying tower to obtain solid particles. Solid particles solidify on the wall of the tower and are removed for particle size classification. Particles larger than about 500 microns are ground further to reduce the particle size by cryogenic grinding with dry ice.

Matrix Perfume Microcapsules

Water-activated matrix perfume microcapsules can be applied to the fluid absorbent articles by uniformly sprinkling, mixing, or distributing the microcapsules onto the fluid absorbent materials. It is preferred to have the perfume microcapsules applied to areas most likely to be wetted by body fluids.

An example of water-activated matrix perfume microcapsules is an IN-CAP microcapsule sample (hereinafter called "Microcapsule 1") obtainable from Polak's Frutal Works, Inc., having about 50% perfume loading and particle size range of from

about 3 microns to about 100 microns. Major components of the perfume are highly volatile components, such as citral and d-limonene.

All percentages, ratios, and parts herein, in the Specification, Examples, and Claims, are by weight and are approximations unless otherwise stated.

The following are non-limiting examples of the instant compositions, articles, and methods.

EXAMPLE 1

A composition of matter suitable for use as an absorbent pad in diapers, sanitary napkins, and the like, comprises a substantially homogeneous blend of the following.

<u>Ingredient</u>	<u>Wt.%</u>
Southern Softwood Kraft Cellulose Fibers	79.7
ValforR CP300-56 Intermediate Zeolite	20
ZnCl ₂	0.3

EXAMPLE 2

A composition of matter suitable for use as an absorbent pad in diapers, sanitary napkins, and the like, comprises a substantially homogeneous blend of the following:

<u>Ingredient</u>	<u>Wt.%</u>
Southern Softwood Kraft Cellulose Fibers	79.7
Beta-Cyclodextrin	20
ZnCl ₂	0.3

EXAMPLE 3

A pad suitable for use as an absorbent structure in diapers, sanitary napkins, and the like, is prepared as follows. Twenty parts of beta-cyclodextrin and 1 part of ZnCl₂ are dissolved in about 200 parts of distilled water at about 70°C into a clear solution. This solution is sprayed on about 200 parts of Kraft cellulose fibers and allowed to dry. The resulting pad contains small particles of cyclodextrin which are attached to the cellulose fibers.

EXAMPLE 4

A pad suitable for use as an absorbent structure in diapers, sanitary napkins, and the like, is prepared as follows. About 1 part of beta-cyclodextrin and about 4 parts of polyethylene glycol of average molecular weight (MW) of about 3,400 are dissolved in about 240 parts of distilled water at about 70°C into a clear solution. This solution is sprayed on about 200 parts of Kraft cellulose fibers. The water is then removed by freeze drying. The resulting pad contains small particles of cyclodextrin which are attached to the cellulose fibers.

EXAMPLE 5

A composition of matter suitable for use as an absorbent pad in diapers, sanitary napkins, and the like, is prepared as follows. About 1 part of aqueous ZnCl₂ solution (50% solids) is sprayed uniformly on about 60 parts of Kraft cellulose fibers and allowed to dry. About 18 parts of solid beta-cyclodextrin/polyethylene glycol Particles 1 are dry mixed with the cellulose fibers. The resulting mixture is placed in an 80°C oven for about 5 minutes to attach the solid particles to the cellulose fibers.

EXAMPLE 6

A composition of matter suitable for use as fluid and odor absorbent materials in diapers, sanitary napkins, and the like, is prepared as follows. About 1 part of aqueous ZnCl₂ solution (50% solids) and about 50 parts of Mixed Perfume Complex/Cyclodextrin Slurry 1 are sprayed uniformly on about 100 parts of an acrylic acid grafted starch hydrogel having an average particle size of about 250 microns ("Sanwet IM 1000" from Sanyo Co., Ltd. Japan). The resulting mixture is placed in an 80°C oven to dry. The mixture is cooled and comminuted, if needed, to produce the absorbent materials.

EXAMPLE 7

A lightweight pantiliner suitable for use between menstrual periods, and which can be disposed of in a toilet (i.e., "flushable") comprises a pad (surface area about 117 cm²); with about 4 g of the composition of Example 2, said pad being interposed between the topsheet of U.S. Pat. No. 4,463,045, supra, and a fibrous, nonwoven, flushable backsheet.

EXAMPLE 8

A catamenial product in the form of a sanitary napkin having two flaps extending outward from its absorbent core is prepared using the pad of Example 3 (surface area about 117 cm²); per the design of U.S. Pat. No. 4,687,478, Van Tillburg, issued Aug. 18, 1987. The nonglossy sheet of U.S. Pat. No. 4,463,045, supra, is used as the topsheet.

EXAMPLE 9

A disposable baby diaper using the odor-control pad of Example 4 is prepared as follows. The dimensions listed are for a diaper intended for use with a child in the 6-10 kilogram size range. These dimensions can be modified proportionately for different size children, or for adult incontinence briefs, according to standard practice.

1. Backsheet: about 0.025-0.070 mm polyethylene; width at top and bottom about 33 cm; notched inwardly on both sides to a width-at-center of about 28.5 cm; length about 50.2 cm.

2. Topsheet: tapered capillary polyethylene topsheet, per U.S. Patent 3,929,135, described hereinabove; width at top and bottom about 33 cm; notched inwardly on both sides to a width-at-center of about 28.5 cm; length about 50.2 cm.

3. Absorbent core: air-laid wood pulp fibers per Example 4, about 8.4 mm thick, calendered; width at top and bottom about 28.6 cm; notched inwardly at both sides to a width-at-center of about 10.2 cm; length about 44.5 cm; with about 0.7 g of ZnCl₂ and about 1.45 g of beta-cyclodextrin dispersed in said core.

4. Elastic leg bands: four individual rubber strips (2 per side); width about 4.77 mm; length about 370 mm; thickness about 0.178 mm (all the foregoing dimensions being in the relaxed state).

The diaper of Example 9 is prepared in standard fashion by positioning the core-plus-odor control material and scent signal covered with the topsheet on the backsheet and gluing.

The elastic bands (designated "inner" and "outer," corresponding to the bands closest to, and farthest from, the core, respectively) are stretched to about 50.2 cm and positioned between the topsheet/backsheet along each longitudinal side (2 bands per side) of the core. The inner bands along each side are positioned about 55 mm from the narrowest width of the core (measured from the inner edge of the elastic band). This provides a spacing element along each side of the diaper comprising the flexible topsheet/ backsheet material between the inner elastic and the curved edge of the core. The inner bands are glued down along their length in the stretched state. The outer bands are positioned about 13 mm from the inner bands, and are glued down along their length in the stretched state. Since the topsheet/backsheet assembly is flexible, the glued-down bands contract to elasticize the sides of the diaper.

EXAMPLE 10

A disposable baby diaper is made similarly to that of Example 9, except that the absorbent core comprises a pad of wood pulp fibers of Example 5.

What is claimed is:

1. An absorbent composition which minimizes the odor that can be caused by bodily fluids and which optionally provides a scent signal indicating that the odor is being removed, comprising:
 - I. an effective amount of material that inhibits the formation of odor that has at least one attribute selected from the group consisting of antimicrobial activity, urease inhibition activity, pH adjustment activity, and mixtures thereof;
 - II. an effective amount of odor-absorbing material for objectionable odor molecules
 - III. optionally, an effective amount of moisture-activated encapsulated perfume; and
 - IV. an effective amount of fluid absorbing material.
2. The composition of Claim 1 wherein said odor absorbing material is selected from the group consisting of:
 - A. cyclodextrin, optionally beta-cyclodextrin;
 - B. zeolite, optionally intermediate silicate/aluminate zeolite having a SiO₂/AlO₂ molar ratio of less than about 10;
 - C. activated carbon;
 - D. kieselguhr;
 - E. acid salt forming materials; and
 - F. mixtures thereof;
3. The composition of Claim 1 or Claim 2 wherein the odor-absorbing material is a mixture of activated carbon and zeolite wherein the carbon is optionally coated with the zeolite.
4. The composition of any of Claims 1-3 wherein the fluid absorbing material is selected from the group consisting of (1) fibrous absorbent material, optionally selected from the group consisting of cotton fluff, cellulose pulp, chemithermomechanical pulp, citric acid cross-linked cellulose pulp, synthetic fibers, and mixtures thereof; (2) absorbent gelling material, optionally selected from the group consisting of: (a) hydrolyzed polyacrylate gelling material; (b) hydrolyzed polyacrylate grafted starch gelling material; (c) hydrolyzed polyacrylonitrile grafted starch; (d) maleic anhydride-isobutylene copolymers; and (e) mixtures thereof; (3) absorbent foam, (4) absorbent sponge, and (5) mixtures thereof.

5. The composition of Claim 4 wherein the absorbent gelling material is (a), (b), and mixtures thereof.

6. The composition of any of Claims 1-5 wherein the perfume is selected from the group consisting of highly volatile perfume, moderately volatile perfume, and mixtures thereof, preferably highly volatile perfume.

7. The composition of any of Claims 1-6 wherein the moisture-activated encapsulated perfume is selected from the group consisting of (1) cyclodextrin/perfume inclusion complexes, said complexes preferably having a major portion with a particle size of less than about 10 microns, more preferably less than about 8 microns, and even more preferably less than about 5 microns; (2) solid cellular matrix perfume microcapsules, and (3) mixtures thereof.

8. An article of manufacture selected from the group consisting of:

- (a) catamenials;
- (b) pantiliners;
- (c) diapers;
- (d) adult incontinence garments; and
- (e) underarm shields;

comprising an effective amount of the composition of any of Claims 1-7.

9. The article of Claim 8 wherein the level of odor-absorbing material, preferably cyclodextrin, intermediate silicate/aluminate zeolite having a $\text{SiO}_2/\text{AlO}_2$ molar ratio of less than about 10, and/or mixture of activated carbon and zeolite, said carbon optionally being coated with the zeolite, is from about 0.1 g to about 10.0 g per article.

10. The article of Claim 8 or Claim 9 wherein the fluid absorbing material is selected from the group consisting of (1) fibrous absorbent material, preferably fibrous absorbent material is selected from the group consisting of cotton fluff, cellulose pulp, chemithermomechanical pulp, citric acid cross-linked cellulose pulp, synthetic fibers, and mixtures thereof; (2) absorbent gelling material, optionally selected from the group consisting of: (a) hydrolyzed polyacrylate gelling material; (b) hydrolyzed polyacrylate grafted starch gelling material; (c) hydrolyzed polyacrylonitrile grafted starch; (d) maleic anhydride-isobutylene copolymers; and (e) mixtures thereof, more preferably (a) and/or (b); (3) absorbent foam, (4) absorbent sponge, and (5) mixtures thereof.